Final Technical Report on Grant

AFOSR-87-0045

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A multi-nuclear, high resolution, high field NMR spectrometer system equipped with wide-bore (89 mm) 7.05 Tesla superconducting magnet, and accessories for high resolution solid state work and an NMR data station were funded under this instrumentation grant.

The basic system, a General Electric GN-300, was installed in September, 1986. The necessary accessories for high resolution NMR work on solids were installed during the week of February 23-28, 1987. The new Nicolet 1280 NMR data system, delivered in October 1986, is currently being used to control a recently built specialized NMR spectrometer using a wide bore 4.2 Tesla superconducting magnet made by Oxford Instruments.

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1. Instrumentation Grant AFOSR 87-0045

The DOD instrumentation proposal ARO-DOD-URIP-Control No. 860314 was submitted via the AFOSR and $370,000 was awarded under the grant AFOSR-87-0045 for the purchase of "High Field, High Resolution NMR Spectrometer with Accessories." We purchased General Electric GN-300 NMR spectrometer with accessories. The NMR spectrometer was installed in February 1987, and its performance exceeds the specifications. The technical specifications of the GN-300 NMR spectrometer are given in Section 2. The actual equipment purchased under the grant is given in Section 3.

The NMR spectrometer and its accessories work well and are in daily use since the installation. So far the acquisition of the NMR spectrometer enabled us to carry out research supported by the AFOSR under the grant AFOSR-85-0345. The list of publications which resulted from the use of the NMR spectrometer is given in Section 4. Section 5 includes the Appendix with the Interim Report on Grant AFOSR 87-0045.

2. Technical Specifications for the GN-300 Spectrometer System with Accessories

GN-300

Technical Specifications

Oxford Cryomagnet:

* 7.05 Tesla field strength
* 89mm room temperature bore
* 25ml/hr He boil-off rate
* 250ml/hr N_2 boil-off rate
* N_2 refill capacity 60 liters
* He refill capacity 25 liters
* He refill interval is at least 40 days
* N_2 refill interval is at least 10 days
* Computer-monitored liquid N_2 and He levels

Data System:

* Nicolet 1280 computer
* 128K data table standard with optional 256K data table
* 20 bits/word
* 8-color raster scan display
* 8-color digital plotter
* Keyboard
* Standard 12-bit digitizer with $\pm$ 62.5 kHz spectral width
* Standard 32-Mbyte CDC disk drive with 16 Mbytes fixed
* Optional 16-bit digitizer with $\pm$ 12.5 kHz spectral width
* Optional 12-bit digitizer with $\pm$ 500 kHz spectral width
* RS-232C interface ports
* Optional 128K word array processor
* Optional 96-Mbyte CDC disk drive with 80 Mbytes fixed

Front Panel:

* 3 multifunctional computer-readable knobs
* Observe and decoupler status LED's
* 3 manual shim knobs
* Lock level meter

Observe System:

* Broadband range between 5 and 300 MHz in 1 Hz steps
* Recovery time is less than 5 usec
* 15^{o} digital transmitter phase shifts $\pm$ 1^{o}
* Continuously variable computer-controlled transmitter phase shift interpolator greater than 15^{o} under programmable pulser control
* Phase shift time is less than 1 usec

Audio Filter:

* $\pm$ 50 Hz to $\pm$ 100 kHz in 100 Hz steps or $\pm$ 500 kHz

Lock:

* Internal deuterium lock
* Computer-controlled autolock or manual control
* Minimum lock concentration, 2% $CDCl_3$ in 10mm and 10% in 5mm tubes

Decoupler (Proton):

* Computer control of all parameters
* Output 20W
* Digital attenuator 0 to 82 dB in 1 dB steps
* Frequency resolution of 0.397 Hz; optional 0.0417 Hz available
* $\pm$ 40-kHz offset capability
* 15^{o} digital phase shift $\pm$ 1^{o}
* Continuously variable computer-controlled phase shift greater than 15^{o} under programmable pulser control
* ROM-stored modulation schemes control 90^{o}- and 180^{o}-phase shifts
* Other programmable pulser modulation schemes, (e.g. amplitude and phase modulation), possible
* Phase shift and attenuator switching time less than 2 usec

Room Temperature Shim Power Supply:

* 18 computer-controlled shims with three manual front panel controls for Z1, Z2 and Z3 shims

Air Control:

* Air flow meters and valves for eject air, body air, spinner air and variable temperature (VT) air
* Computer-controlled spinner air flow valve
* Computer-controlled solenoids for eject air, VT air and body air

Variable Temperature:

* Microprocessor-controlled variable temperature unit
* 0.1° C resolution
* VT range -200° to +300° C, (-100° to +160° C standard probe range)

Power Amplifiers:

* Decoupler power amplifier with 20W proton output
* 5 to 200 MHz observe power amplifier at 100W
* $^{1}H/^{19}F$ observe power amplifier at 100W
* Observe low power amplifier 5 to 320 MHz at 1W
* Computer-controlled digital attenuator for observe power covers 63 dB in 1 dB steps

Probe Interface Module:

* Computer-switchable between $^{1}H/^{19}F$ and X nuclei observe
* Integral tuning bridge with raster display

Programmable Pulser:

* Pulse width outputs 160 nsec to 10,000 sec (3 hrs.)
* Timing resolution 10 nsec
* 40 independent pulse lines
* 256 programmable intervals
* Versatile looping capability
* Variable loop counter
* Conditional jump feature
* Easily user-programmed

Microprocessor-controlled System Monitor:

* Monitors all shim currents
* Monitors all critical power supplies
* Monitors forward and reverse decoupler power
* Monitors lock level
* Monitors cryogen levels

Optional Chemagnetics CPMAS Accessory:

* Resolution of less than 3 Hz on adamantane
* Sensitivity of greater than 200:1 on 8 scans Hexamethylbenzene
* Optional variable temperature range of -150° to +30° C
* Optional variable angle (0°-90°) spinning
* Multinuclear capability of ^{31}P to ^{15}N

Performance Specifications for GN-300WB

		Lineshape	Resolution	S/N	Sample	Pulse 90 deg
A.	5mm 1H/13C					
	1. 1H	15/35	0.3	100:1	0.1% EB	10
	2. 13C	6/15	0.2	80:1	ASTM	15
	3. Gamma H*2 = 10kHz @ 10W					
B.	10mm BB 31P to 15N					
	1. 31P		0.2	280:1	1% TMP	25
	2. 13C	6/15	0.2	300:1	ASTM	25
	3. 2H		0.2	30:1	H20	35
	4. 17O			150:1	H20*	40
	5. 15N		0.3	20:1	90% Form w/o NOE	50
	6. Gamma H*2 = 6kHz @ 20W					
C.	10mm BB 73Ge to 15N					
	1. 15N		0.3	30:1	90% Form w/o NOE	50
	2. 14N			60:1	.5M NH4Br	60
	3. 73Ge			50:1	90% GeCl4	70
	4. Gamma H*2 = 5kHz @ 20W					

3. Equipment Purchased

Catalog Number	Description	Price
881-007800	GN-300 - The General Electric GN-300 is a high performance multi-nuclear NMR spectrometer capable of observing all nuclei from 73Ge to 1H. The basic system is comprised of a 7.05T superconducting magnet, RF electronics, and a data system based on the Nicolet 1280 computer. The standard software package allows simultaneous data acquisition, processing and plotting for increased sample throughput. Other features are user definable macro instructions, fully automated locking, shimming and phasing of spectra, automated relaxation time measurement, curve fitting and analysis routines, and two dimensional contour plotting. Basic, Pascal, and Fortran compilers are also included.	$304,750.00
Accessories		
869-015200	12 Bit Digitizer, Dual Channel 250 kHz Data Rate	2,750.00

869-019200	86 Mbyte Disk, 1 Mbyte floppies	12,500.00
843-010400	10 mm ^{31}P - ^{15}N Tunable Probe	12,000.00
869-018600	Array Processor	10,000.00
869-050100	CPMAS V. T. 9.5mm Highband Probe	22,500.00
869-050400	CPMAS V. T. 9.5mm Lowband Probe	22,500.00
869-053200	CPMAS Probe Interface (one required)	1,000.00
869-052700	30-80 MHz Observe Amplifier	6,000.00
869-052800	55-125 MHz Observe Amplifier	6,000.00
869-052900	300 MHz Decoupling Amplifier	4,000.00
841-012700	Accessory Console	3,000.00
841-012100	Micro-Processor Controlled Temperature Unit	12,000.00
869-051100	V. T. Controller Heater	7,000.00
	Total Price for Above Accessories	126,300.00
	Total System Price	431,000.00
	Less 20% Discount	86,200.00
	Total System Price	$344,800.00

Selected Components for NIC 1280 NMR Data System

869-011200	Zeta 8 Plotter	$ 8,500.00
884-000600	Cabinet	3,000.00
869-011500	CMD, 96 Mbyte disk 1180 Systems	18,500.00
869-021100	CMD, 1280 Interface	3,500.00
869-01800	256K Memory - 1280 only	8,000.00
869-010900	Raster Scan Monitor	6,500.00

869-000800	Model 43 Teletype	2,330.00
869-008400	12-bit digitizer	2,750.00
	Total Price	53,080.00
	Less Discount (-52%)	27,601.60
	Total NMR Data System	25,478.40
	Grand Total Instrument Price	$370,273.40

4. List of Publications which Resulted from the Acquisition of the NMR Spectrometer System

"NMR Studies of Mixed Alkoxide Systems," J. Jonas, A. D. Irwin and J. S. Holmgren, Third International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites, Ed. J. D. Mackenzie and D. R. Ulrich (J. W. Wiley, NY), 1987.

"Preparation of Borosilicate Gels Under Anhydrous Conditions," J. B. Chan, P. J. Grandinetti, J. S. Holmgren and J. Jonas, J. Non-Crystalline Solids, submitted.

"Solid State ^{29}Si NMR Study of Polycondensation During Heat Treatment of Sol-Gel Derived Silicas," A. D. Irwin, J. S. Holmgren and J. Jonas, Mat. Lett. 6, 25 (1987).

"Solid State ^{29}Si and ^{11}B NMR Studies of Sol-Gel Derived Borosilicates," A. D. Irwin, J. S. Holmgren and J. Jonas, J. Non-Crystalline Solids, in press.

"^{27}Al and ^{29}Si NMR Study of Sol-Gel Derived Aluminosilicates and Sodium Aluminosilicates," A. D. Irwin, J. S. Holmgren and J. Jonas, J. of Materials Science, in press.

"The Effect of Fluoride on the Sol-Gel Process," R. Winter, J. B. Chan, R. Frattini and J. Jonas, Manuscript in preparation.

5. Appendix - Interim Report

APPENDIX

Interim Report on Grant

AFOSR-85-0045

Period Covered: October 1, 1986 to March 27, 1987

PRINCIPAL INVESTIGATOR

Name: Jiri Jonas Department: Chemistry

Title: Professor Address: 166 Roger Adams Lab

Social Security No. 331-40-6560 Telephone No.: (217) 333-2572

University of Illinois

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Urbana, Illinois 61801

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1. Summary of Instrumentation Obtained

A multi-nuclear, high resolution, high field NMR spectrometer system equipped with wide-bore (89 mm) 7.05 Tesla superconducting magnet, and accessories for high resolution solid state work and an NMR data station were funded under this instrumentation grant.

The basic system, a General Electric GN-300, was installed in September 1986. This instrument is a high performance multi-nuclear NMR spectrometer capable of observing all nuclei from ^{73}Ge to ^{31}P, as well as ^{1}H. The basic system is comprised of a 7.05 Tesla superconducting magnet, RF electronics, and a data system based on the Nicolet 1280 computer.

The necessary accessories for high resolution NMR work on solids were installed during the week of February 23-28, 1987. Only the variable temperature accessory for the solid state work remains undelivered.

The new Nicolet 1280 NMR data system, delivered in October 1986, is currently being used to control a recently built specialized NMR spectrometer using a wide-bore 4.2 Tesla superconducting magnet made by Oxford Instruments.

2. Detailed Equipment Listing

2.1 Manufacturer

General Electric Company
Medical Systems Group
P.O. Box 4905
255 Fourier Avenue
Fremont, CA 94539
(415) 490-8310

2.2 Equipment Requested

Catalog Number	Description	Price
881-007800	GN-300 - The General Electric GN-300 is a high performance multi-nuclear NMR spectrometer capable of observing all nuclei from 73Ge to 1H. The basic system is comprised of a 7.05T superconducting magnet, RF electronics, and a data system based on the Nicolet 1280 computer. The standard software package allows simultaneous data acquisition, processing and plotting for increased sample throughput. Other features are user definable macro instructions, fully automated locking, shimming and phasing of spectra, automated relaxation time measurement, curve fitting and analysis routines, and two dimensional	$304,750.00

contour plotting. Basic, Pascal, and Fortran compilers are also included.

Accessories

869-015200	12 Bit Digitizer, Dual Channel 250 kHz Data Rate	$ 2,750.00
869-012100	CDC 32 Mbyte Disk, 16 Mbyte Removable; 115V, 60 Hz	14,500.00
843-010100	5 mm $^{1}H/^{13}C$ Dual Probe	13,000.00
843-010400	10 mm ^{31}P - ^{15}N Tunable Probe	12,000.00
843-010500	10 mm ^{15}N - ^{73}Ge Tunable Probe	12,000.00
869-018600	Array Processor	10,000.00
869-050100	CPMAS 9.5mm Highband Probe	19,500.00
869-050400	CPMAS 9.5mm Lowband Probe	19,500.00
869-053200	CPMAS Probe Interface (one required)	1,000.00
869-051400	Cables/Plug-in for ^{29}Si	1,000.00
869-052100	Cables/Plug-in for ^{11}B	1,000.00
869-052500	Cables/Plug-in for ^{17}O	1,000.00
869-052700	30-80 MHz Observe Amplifier	6,000.00
869-052800	55-125 MHz Observe Amplifier	6,000.00
869-052900	300MHz Decoupling Amplifier	4,000.00
869-053100	RF Monitor Panel	4,000.00
841-012700	Accessory Console (Required)	8,000.00
	Total Price of Above Accessories	$135,250.00
	Total System Price with Above Accessories	$440,000.00

2.3 Equipment Purchased

Catalog Number	Description	Price
881-007800	GN-300 - The General Electric GN-300 is a high performance multi-nuclear NMR spectrometer capable of observing all nuclei from 73Ge to 1H. The basic	$304,750.00

system is comprised of a 7.05T superconducting magnet, RF electronics, and a data system based on the Nicolet 1280 computer.
The standard software package allows simultaneous data acquisition, processing and plotting for increased sample throughput. Other features are user definable macro instructions, fully automated locking, shimming and phasing of spectra, automated relaxation time measurement, curve fitting and analysis routines, and two dimensional contour plotting. Basic, Pascal, and Fortran compilers are also included.

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869-050400	CPMAS V. T. 9.5mm Lowband Probe	22,500.00
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869-052800	55-125 MHz Observe Amplifier	6,000.00
869-052900	300 MHz Decoupling Amplifier	4,000.00
841-012700	Accessory Console	8,000.00
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869-051100	V. T. Controller Heater	7,000.00
	Total Price for Above Accessories	126,300.00
	Total System Price	431,000.00
	Less 20% Discount	86,200.00
	Total System Price	$344,800.00

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884-000600	Cabinet	3,000.00
869-011500	CMD, 96 Mbyte disk 1180 Systems	18,500.00
869-021100	CMD, 1280 Interface	3,500.00
869-01800	256K Memory - 1280 only	8,000.00
869-010900	Raster Scan Monitor	6,500.00
869-000800	Model 43 Teletype	2,330.00
869-008400	12-bit digitizer	2,750.00
	Total Price	53,080.00
	Less Discount (-52%)	27,601.60
	Total NMR Data System	25,478.40
	Grand Total Instrument Price	$370,278.40

2.4 Explanation of Changes to the Equipment List

a. Requested

869-012100 CDC 32 Mbyte Disk, 16 Mbyte Removable;
115V, 60 Hz
$14,500.00

Purchased

869-619200 86 Mbyte Disk, 1 Mbyte floppies
$12,500.00

Remarks

The larger internal disk (86 Mbyte vs. 32 Mbyte) will facilitate manipulations of 2-D NMR data. Floppy diskettes can be archived more easily.

b. Requested

843-010100 5 mm $^{1}H/^{13}C$ Dual Probe
$13,000.00

Remarks

$^{1}H/^{13}C$ NMR spectra can be run on the 10 mm ^{31}P-^{15}N tunable probe.

c. Requested

843-010500 — 10 mm ^{15}N - ^{73}Ge Tunable Probe
$12,000.00

Remarks

Obtained as a donation from G.E.

d. Requested

869-051400 — Cables/Plug-in for ^{29}Si
$1,000.00

869-052100 — Cables/Plug-in for ^{11}B
$1,000.00

869-052500 — Cables/Plug-in for ^{17}O
$1,000.00

869-053100 — RF Monitor Panel
$4,000.00

Remarks

Built at the University of Illinois for a total cost of $1,500.00.

e. Requested

869-050100 — CPMAS 9.5 mm Highband Probe
$19,500.00

869-050400 — CPMAS 9.5 mm Lowband Probe
$19,500.00

Purchased

869-050100 — CPMAS VT 9.5 mm Highband Probe
$22,500.00

869-050400 — CPMAS VT 9.5 mm Lowband Probe
$22,500.00

841-012100 — Micro-Processor Controlled Temperature Unit
$12,000.00

869-051100 — V. T. Controller Heater
$7,000.00

Remarks

Variable temperature capability is essential in the study of dynamic processes.

3. Sol-Gel Process

3.1 B_2O_3-SiO_2

Previously, in studies involving the borosilicate sol-gel system, we were able to show, using ^{11}B and ^{29}Si NMR spectroscopy as well as infrared spectroscopy, that although some borosiloxane (≡B-O-Si≡) linkages are formed in solution the majority of the necessary borosiloxane linkages form during the thermal treatment [1]. We are currently conducting further spectroscopic studies on this borosilicate sol-gel system using ^{11}B and ^{29}Si MAS and CPMAS NMR. Through these studies we hope to better understand the condensation which leads to the formation of ≡B-O-Si≡ during the drying and subsequent heat treatment of these gels.

3.2 Al_2O_3-SiO_2 and Na_2O-Al_2O_3-SiO_2

During the past year we have developed procedures to prepare homogeneous aluminosilicate gels over a wide range of compositions [2]. We are currently performing spectroscopic studies using ^{27}Al and ^{29}Si MAS and CPMAS NMR to determine the chemical and structural nature of the products. We are particularly interested in the chemical environment of the aluminum atoms and the dependence of this environment on compositional and processing variables. The ultimate goal of these studies is to further our understanding of how we may use processing parameters to influence the final properties of these materials [3].

3.3 TiO_2-SiO_2 and ZrO_2-SiO_2

Feasibility studies on the use of $^{47,49}Ti$, ^{91}Zr and ^{17}O NMR spectroscopy in the study of the sol-gel process are in progress. We are particularly interested in studying the hydrolysis and condensation stages of the mixed alkoxide systems: TiO_2-SiO_2 and ZrO_2-SiO_2. Due to the quadrupolar nature of these nuclei, however, we find that complementary studies using ^{29}Si NMR are essential. We are currently persuing the latter.

4. Viscous Fluids

The viscous fluid, 2-ethylhexylbenzoate, is currently the object of extensive study as it is a model lubricant. In preparation for high pressure NMR studies, ^{13}C spin lattice relaxation times (T_1's) and nuclear Overhauser enhancements (NOE's) were recorded as a function of temperature between -34.8°C and 103°C using the GN-300 [4].

References

[1] A. D. Irwin, J. S. Holmgren, T. W. Zerda and J. Jonas, J. Non-Crystalline Solids 89, 191 (1987).

[2] J. Jonas, A. D. Irwin, J. S. Holmgren, in Third International Conference on Ultrastructure Processing of Ceramics, Glasses and Composites, Ed. J. D. Mackenzie and D. R. Ulrich (J. W. Wiley, NY), 1987, to be published.

[3] A. D. Irwin, J. S. Holmgren, J. Jonas, Manuscript in preparation.

[4] N. Walker, J. Jonas, Manuscript in preparation.